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(54) Title: IMPROVED METHOD FOR BONDING COPPER TO A POLYMERIC MATERIAL

(57) Abstract

The present invention provides an improved method for preparing multilayer copper/polymer composite materials. More specifically, the improved method of the present invention is directed toward a process involving the steps of (1) oxidizing the surface of a copper layer with an alkaline oxidizing solution; (2) reducing the oxidized surface of the copper layer with a reducing solution such as a solution of an amine borane; (3) passivating the reduced surface of the copper layer with a passivating solution such as an aqueous or non-aqueous solution of 2-mercaptobenzothiazole or its soluble salts; and (4) bonding a polymer layer to the treated surface of the copper layer to form a multilayer copper/polymer composite material.

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"Improved Method for Bonding Copper to a Polymeric Material"

BACKGROUND OF THE INVENTION

The present invention is directed to an improved method for bonding a layer of copper or copper alloy to a layer of polymeric material, such as in the manufacture of multi-layer printed circuit boards or printed wiring boards (hereinafter "multi-layer circuit boards"). More particularly, the present invention stabilizes and maintains ("passivates") the reduced surface of a previously oxidized layer of copper or a copper alloy. As a result of this passivation, the surface of the copper or copper alloy becomes resistant both to further oxidation and subsequent chemical attack by acids (dissolution). This treatment increases the ability of the reduced copper surface to bond to a polymer layer and to maintain inter-layer adhesion in printed circuit or printed wiring boards. The present invention is useful because it enables manufacturers of printed circuit boards and printed wiring boards to store and heat treat reduced layers of copper or a copper alloy without loss of the chemical identity or integrity of the reduced surfaces.

Multi-layer metal/polymer materials are used extensively in the manufacture of both printed wiring boards and printed circuit boards for data processing equipment. Printed wiring boards must have a very high wiring density to satisfy today's needs for increased capacity and processing speed. These requirements result in an increased number of layers in these multi-layer materials, up to twenty or more, and reduced wiring grid size and line width. To meet these demanding requirements, the multi-layer materials must have a high degree of accuracy in layer registration. In addition, both printed wiring boards and printed circuit boards, hereinafter referred to collectively as

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printed circuit boards, have demanding requirements for inter-layer adhesion.

A number of methods have been developed to improve inter-layer adhesion between copper and polymers. Many of these methods involve the application or creation of surface coatings on the copper layers. For example, different colored oxide coatings, such as a black or a brown oxide layer, can be created on the surface of the copper layer by immersing the copper in a heated alkaline solution of an oxidizing agent such as sodium chlorite.

The oxide coating on a copper surface results in a roughened surface topography. This rough topography is characterized by an increase in surface area on the copper layer. It is believed that this increase in surface area is responsible for increased adhesion between the treated copper layer and the polymeric layer in the composite material that results.

However, the existence of an oxide coating on the surface of the copper layer can cause inter-layer adhesion problems in the resulting composite material. The oxide coating on the surface of the copper layer is much more brittle than the bare metal surface and is prone to fracture when subjected to stresses. In the fabrication of a multi-layer printed circuit board, it is customary to drill holes through the composite material. The stresses accompanying the drilling process can cause fracture of the oxide coating on the metal layer. This results in sites within the multi-layer material which can lead to failures in inter-layer adhesion.

The loss of structural integrity in the oxide coating on copper layers within the multi-layer material also leads to further problems affecting inter-layer adhesion strength. Often, after

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drilling in the printed wiring or circuit board manufacturing process, the composite material is subjected to further chemical treatments which include exposure to acidic solutions either for 5 cleaning or in subsequent plating operations. The copper oxides on the copper layers are susceptible to attack by aqueous acids, and eventual dissolution. Any mechanical failures in the oxide layer from drilling provide a means for an acid solution to attack further into the inter-layer 10 regions of the material, weakening adhesion between the layers. This condition is manifest by a pink annular region surrounding the site of drilling. In the art, this phenomenon is referred 15 to as "pink ring." Attempts have been made to minimize the frequency and the magnitude of the pink ring phenomenon by optimizing the polymer bonding, drilling, cleaning, and plating processes. However, these attempts have met with only 20 limited success and have failed to consistently or completely prevent occurrence of the phenomenon.

For example, U.S. Patent No. 4,642,161 discloses a method of bonding copper and a polymer resin which involves enhancing bonding between the 25 copper and polymer layers through chemically reducing the copper(II) oxide coating that is formed on the copper layer after an oxidation step. According to the '161 patent, the oxide coating is reduced to metallic copper through 30 treatment with a solution of an amine borane. The reduced copper surface is said to exhibit the resistance of copper metal to dissolution by acids while retaining the roughened topography of the oxide layer for enhanced bonding to a polymer 35 layer.

However, as often occurs in industry, copper layers reduced according to the method of the '161 patent may not immediately be bonded to a polymer

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layer. The delay between treatment and bonding may extend to several days or longer. As a result of this delay, the reduced surface of the copper inevitably re-oxidizes through reaction with atmospheric oxygen. Moreover, the reduced copper layer is often subject to baking at elevated temperatures before subsequent fabrication steps. As a result, the reduced surface, which is exposed to atmospheric oxygen, will re-oxidize at an accelerated rate. This can be avoided through vacuum drying or the use of drying ovens with inert atmospheres, but only with a considerable increase in total treatment costs due to the highly specialized and expensive equipment needed.

Accordingly, it is an object of the present invention to passivate a reduced, or substantially reduced surface of a copper layer that is used in the manufacture of multi-layer printed circuit or printed wiring boards.

Another object of the present invention is to provide a process to treat a partially oxidized surface of a copper layer so that the treated surface will be less susceptible to further oxidation or to chemical attack by aqueous solutions of mineral acids.

SUMMARY OF THE INVENTION

The present invention provides an improved method for preparing alternately layered copper/polymeric materials, preferably layered or multi-layered circuit boards. More specifically, the improved method of the present invention is directed toward a process involving the steps of (1) oxidizing the surface of a layer of copper or copper alloy; (2) reducing the oxidized surface of the copper or copper alloy to a lower oxidation state or a mixture of low oxidation states; (3) passivating the reduced surface of the copper

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or copper alloy; and (4) bonding the reduced and passivated surface of the copper or copper alloy to the surface of a polymeric layer.

The layered and multi-layer copper/polymer materials formed by the method of the present invention are characterized by resistance to the formation of "pink ring" which is associated with the failure of inter-layer adhesion. Practice of the present invention prevents or minimizes the occurrence of this undesirable phenomenon.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an improved method for bonding a layer of copper or copper alloy to a polymer layer. In its broadest aspect, the method of the present invention is applicable to improving the bonding between any layer of copper or copper alloy and a polymer layer. Preferably, the improved method of the present invention is used to enhance the bonding between a layer of copper or copper alloy and a polymer layer during the fabrication of a multi-layer electronic circuit board. The improved method of the present invention comprises:

- 1) oxidizing the surface of a layer of copper or copper alloy;
- 2) reducing the oxidized surface of the layer of copper or copper alloy;
- 3) passivating the reduced surface of the copper or copper alloy; and
- 4) bonding the reduced and passivated surface of the copper or copper alloy to the surface of a polymer layer.

A copper or copper alloy layer used in the manufacture of a multi-layer printed wiring or circuit board is subjected to a number of different chemical and physical pretreatment steps that are well known in the art. Initially, the

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surface of the copper or copper alloy layer is cleaned at elevated temperatures in an alkaline solution to remove dirt, surface grease, oils and other contaminants. Subsequent to the cleaning step, the metal layer is rinsed with water and then immersed in an acidic neutralizing solution, followed by another water rinse.

Prior to utilizing the method of the present invention, the copper or copper alloy layers are preferably subjected to an etching process which involves immersing the copper or copper alloy in a solution of a sulfuric acid/hydrogen peroxide mixture, ferric chloride, sodium persulfate, ammonium persulfate, or cupric chloride, followed by a water rinse. This step is a preliminary step which etches or dissolves surface layers of metal atoms and any contaminants remaining on the copper or copper alloy layer from the initial cleaning steps. This treatment would normally be performed at temperatures in the range of room temperature to about 150° F depending upon the etchant. The cleaning, neutralizing and etching steps are all performed with commercially available formulations whose compositions are well known in the art. These preliminary treatments do not constitute the inventive concept incorporated in the subject matter of this application.

In the improved method of the present invention, the surface of the copper or copper alloy layer is first oxidized, preferably with an oxidizing solution. A typical oxidizing solution is an aqueous alkaline solution, preferably pH 8 or greater, of an oxidizing agent such as sodium chl rite or potassium persulfate. Typical concentrations for the oxidizing agents would be in the range f 2 to 200 grams per liter. An alkaline pH is obtained by dissolving from 1 to 50 grams per liter of sodium hydroxide. The copper

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or copper alloy layer is immersed in the oxidizing solution for one to ten minutes at approximately 130° to 200° F. Preferably, the oxidation step also is followed by a water rinse and optional air drying at elevated temperatures in the range of 220° to 320° F. Those of ordinary skill in the art recognize that rinsing and drying steps are used to prevent the contamination and dilution of subsequent reagent baths.

Once the copper or copper alloy layer has undergone the oxidizing treatment step, it is then subjected to a reducing step. The reducing step comprises immersion of the treated metal layer in an aqueous alkaline solution containing an effective amount of a reducing agent such as an aldehyde, a hydrazine, or a sodium borohydride. Typical aqueous reducing solutions and their respective conditions are as follows: immersion in a solution containing 6g/L formaldehyde at 68° F to 140° F for 5 - 30 minutes; immersion in 20% hydrazine at 130° F for 1 - 10 minutes; and immersion in 10g/L of sodium borohydride at room temperature for 3 - 10 minutes. Total immersion time is dependent upon the reducing agent and the temperature of the reducing solution. Generally, higher solution temperatures provide for quicker reduction times.

In addition to the above named compounds, the reducing solution is preferably an alkaline solution of an amine borane with the general formula $BH_3 \cdot NHRR'$, where R and R' are each -H or -CH₃ or -CH₂CH₃. The reduction of the oxide layer on the surface of copper, via an alkaline amine borane solution, is taught in U.S. Patent 4,642,161 which is incorporated herein by reference. Most preferably, the amine borane is dimethylamine borane. When used in the reducing solution, dimethylamine borane is present at a

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concentration effective to result in reduction of the copper or copper alloy. Typically, the concentration of dimethylamine borane is in the range of 5 to 100g/L. A discussion of reducing solutions that employ dimethylamine borane as a reducing agent for copper is taught in U.S. Patent No. 4,642,161, which is incorporated herein by reference.

Preferably, after the reducing step of the present invention, the copper or copper alloy layer is first washed with water and then washed with an aqueous solution containing either a mineral or organic acid and optionally its salt. As would be apparent to one skilled in the art, this additional step neutralizes any residue remaining from the alkaline oxidizing solution. By way of example, "mineral acids" include sulfuric acid, hydrochloric acid or phosphoric acid. A typical neutralization solution that contains a mineral acid is 2% v/v H₂SO₄. By way of example, "organic acids" include oxalic acid, acetic acid, formic acid, citric acid, tartaric acid, phthalic acid and the like. A typical neutralization solution that contains an organic acid is 5g/L citric acid. The copper or copper alloy typically is immersed in this treatment solution for a period of 1 to 2 minutes, preferably one minute, at a temperature in the range of 65 to 140° F. Preferably, this acid neutralization step is followed by a water rinse.

According to U.S. Patent No. 4,642,161, a copper oxide coating that is reduced with an alkaline amine borane is reduced entirely to elemental copper. However, our own experiments using surface spectroscopies, such as x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), reveal that a layer of cupric oxide that is reduced according to the

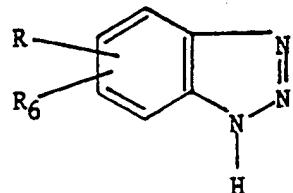
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method of the '161 patent is not totally reduced to metallic copper. Rather, it is reduced to a mixture of elemental copper and cuprous oxide. (See Table 1) During batch operations in circuit board formation, the reduced surface is exposed oftentimes to atmospheric oxygen for 48 to 72 hours at room temperature. After 48 hours of atmospheric exposure, cupric oxide is detected on the reduced surface of the copper layer along with increasing amounts of cuprous oxide. (See the discussion of Table 1 herein.) In the method of the prior art, the reduced surface is typically baked at a temperature within the range of 280° - 320° F to drive off any moisture that would inhibit bonding the layer of copper to a layer of a polymeric material. As a result of the heating, the reduced surface darkens. The darkened surface is cupric oxide as confirmed by its solubility in 17.5% HCl whereupon the darkened copper layer again turns pink. Although baking in an inert atmosphere, such as N₂, would eliminate the oxidation problem, special equipment would be required. Thus, the reduced coating of the '161 patent is still susceptible to the problems which affect inter-layer adhesion.

The third step in the method of the present invention is directed to minimizing the problems that occur with the reduced surface of the copper or copper alloy. In the present invention, the third step passivates or stabilizes the reduced surface on the layer of copper or copper alloy. Passivating involves immersing the copper or copper alloy layer in a solution containing an effective amount of a passivating agent. Suitable compounds for use in the passivating solution include hydroquinone, resorcinol, benzotriazole,

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sodium tolyltriazole, coco imidazoline, 2-ethylhexyl mercaptoacetate or a compound of the formula:



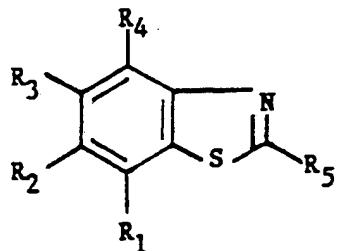
wherein R and R₆ are the same or different and are H, -CH₃ or -C₂H₅. These compounds are present in the passivating solution at concentrations in the range of about 0.1g/L to saturation, preferably at the lower end of the concentration range.

The organometallic compound, Ti[OCH₂CH(C₂H₅)(CH₂)₃CH₃]₄ (i.e., titanium IV 2-ethylhexoxide) is also a useful passivating agent.

Preferably, the passivating agent that is used in the passivating solution will be a compound of the general formula:

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I



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where R₁, R₂, R₃, and R₄ may be the same or different and are either -H, or -CH₃, or -CH₂CH₃; and where R₁ and R₂ act together to form -CH=CH-CH=CH-; or where R₂ and R₃ act together to form -CH=CH-CH=CH-; or where R₃ and R₄ act together to form -CH=CH-CH=CH-; and where R₅ is -OH, -SH, or a corresponding sodium, potassium, lithium, or ammonium salt thereof.

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The passivating solution will contain an effective amount of a passivating agent; preferably an effective amount of a compound of Formula I; more preferably, an effective amount of

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2-mercaptobenzothiazole or a sodium, potassium, lithium or ammonium salt thereof. In the passivating solution, the concentration of 2-mercaptobenzothiazole or its salts is in the range of about 0.1g/L to saturation. For economic reasons, the concentration of 2-mercaptobenzothiazole is preferably at the low end of the concentration range. The compound 2-mercaptobenzothiazole and its sodium salt are commercially available from Pfaltz and Bauer, Waterbury, CT and PMC Specialties, Cincinnati, OH, respectively.

The solvent for the passivating solution is either water, a water soluble non-aqueous solvent or a combination thereof. By the term "water soluble non-aqueous solvent" as used herein is meant any organic solvent that is substantially miscible with water. Preferred water soluble non-aqueous solvents include one or more members of the group consisting of C₁ to C₆ alcohols, C₁ to C₆ glycols, cellosolve (ethylene glycol monoethyl ether), or polyethylene glycols of molecular weight 800 or less, and the like. Such solutions are maintained at an alkaline pH by the addition of sodium or potassium hydroxide, preferably sodium hydroxide, at a concentration of 1.5g/L for a solution containing 0.2g/L of 2-mercaptobenzothiazole. Increasing amounts of 2-mercaptobenzothiazole may require the addition of further hydroxide to effect solution.

A typical passivating treatment consists of immersing the reduced copper or copper alloy layer in the passivating solution at a temperature in the range of 65° to 80° F for a period of from 5 to 30 minutes. The passivating step is best produced within one hour after the reducing step. Increasing amounts of time between the reducing step and the passivating step permit the reduced

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copper surface to slowly re-oxidize due to exposure to atmospheric oxygen. However, this oxidation is relatively small compared to the surface oxidation that occurs when a reduced copper layer that has not been passivated is baked (dried) prior to bonding to a polymeric resin (i.e., a dielectric).

Table 1 summarizes the results of XPS analyses that were performed on three different samples (layers) of copper. The analysis identified the three species of interest: cupric oxide (CuO), cuprous oxide (Cu_2O) and elemental copper (Cu°), at various times and at various depths after oxidizing, reducing and passivating.

Table 1 indicates that after Sample 1 was oxidized using the method of Example 1, 100% CuO was detected both on the surface of the oxidized copper layer and 400 Angstroms (\AA) below the surface. Within about four (4) hours after reduction of the cupric oxide (CuO) layer on Sample 1 using alkaline dimethylamine borane (DMAB), no cupric oxide (CuO) was detected on the surface nor after etching down to 1000 \AA below the surface. Contrary to the teaching in the '161 patent, the DMAB reduction of Sample No. 1 did not result in a complete reduction of all the cupric oxide (CuO) to elemental copper (Cu°), i.e., 58.1% cuprous oxide (Cu_2O) was detected on the surface, whereas about 30-31% Cu_2O was detected below the surface at between 405 - 1000 \AA .

TABLE I
XPS ANALYSIS OF THE SURFACE OF AN OXIDIZED COPPER LAYER
AS A FUNCTION OF SUBSEQUENT TREATMENT AND DEPTH

Copper Sample Number	Surface Depth	Treatment	Hours Last Treatment	CuO	Percentage Cu ₂ O	Cu°
1.	Surface	Oxidation	>48	100%	0	0
1.	400Å	Oxidation	>48	100%	0	0
1.	Surface	Reduction	<4	0	58.1	41.9
1.	405Å	Reduction	<4	0	31.2	68.8
1.	1000Å	Reduction	<4	0	29.6	70.4
2.	Surface	Reduction	>48	22.8	(77.2))
2.	405Å	Reduction	>48	0	46.9	53.1
2.	1000Å	Reduction	>48	0	34.5	65.5
3.	Surface	Reduction and passivation	>48	0	72.7	27.3
3.	405Å	Reduction and passivation	>48	0	"Small Amount"	Majority ¹
3.	1000Å	Reduction and passivation	>48	0	"Small Amount"	Majority ²

¹ Analysis: Cu - 39.47%
 O - 5.63%

² Analysis: Cu - 51.77%
 O - 5.15%

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For copper Sample No. 2 of Table 1, the XPS analysis was performed more than 48 hours after the oxidized copper layer had been reduced via DMAB as above. The difference in XPS analysis between 4 hour post reduction Sample No. 1 and the 48 hour post reduction of Sample No. 2 indicates that the reduced layer of copper oxidized with exposure to atmospheric oxygen. After 48 hours, the surface of Sample No. 2 indicated the presence of 22.8% cupric oxide (whereas Sample 1 had 0%), and increased amounts of cuprous oxide 46.9% and 34.5% at 405Å and 1000Å respectively below the surface. Unlike Sample No. 2, Sample No. 3, which was reduced but soon thereafter passivated, showed no oxidation to cupric oxide even more than 48 hours after reduction and passivation. Further, in Sample No. 3 there was an overall reduced amount of cuprous oxide at 405Å and 1000Å relative to Sample No. 2 notwithstanding that both were tested >48 hours after reduction. Accordingly, the passivation step of the present invention maintained the integrity of a reduced copper layer relative to a copper layer that was reduced but not passivated.

In the prior art, the greatest amount of oxidation to a reduced layer of copper or copper alloy occurs when the reduced layer is baked at temperatures between 220° and 320° F to drive off the moisture prior to bonding to a polymeric or resin layer. However, if the reduced layer of copper or copper alloy is subjected to the passivating step of the present invention, it resists oxidation on exposure to atmospheric oxygen. An oxidized layer of copper that was reduced and passivated according to the present invention exhibited no significant oxidation even after ninety days of exposure to the atmosphere at room temperature. A copper layer that was treated

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with a preferred passivating solution comprising an alkaline solution containing 0.2g/L of 2-mercaptobenzothiazole showed no signs of reoxidizing when baked at about 325° F for 1 hour.

5 Copper layers that were passivated using solutions of the other passivating agents listed above can be heated only to temperatures in the range of 220° - 280° F without showing signs of extensive reoxidation.

10 Between the reducing and passivating step, the capped layer is preferably rinsed to minimize contamination of the passivating solution. After rinsing, the rinsed passivated layer of copper or copper alloy is baked until dry, typically by baking at a temperature between 220° - 320° F for about 1 hour.

15 After drying, the copper or copper alloy layer is bonded to a polymer or resin layer using heat and pressure. The bonding technique is well known to those of ordinary skill in the art. See for example, U.S. Patent 4,775,444 which is incorporated herein by reference. The advantages of the practice of the present invention will be apparent from detailed examination of the examples 20 that follow.

25 A comparison was made for the "pink ring" defect between circuit boards produced by the method of the present invention and circuit boards produced by the same steps but for the reducing and passivating dips. For both methods, the boards were optionally baked at greater than 220° F to drive off any moisture that might interfere with the bonding step. When the boards that were produced by both methods were opened, the board 30 that was produced by the method of reduction 35 without passivation exhibited significant (12-15 mils in radius) "pink ring" around the periphery of the through holes of the circuit

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board. In contrast, the board that was produced by the method of the present invention, wherein the reduced surface was passivated, exhibited no significant "pink ring."

5 Example 1

The surface of a copper layer was oxidized to a black oxide by dipping it for six minutes in a solution at 165° F and comprising 72g/L sodium chlorite, 25g/L NaOH, and 12.5g/L trisodium phosphate dodecahydrate. After the dip, the copper layer was removed and subjected to a running water rinse for two minutes.

10 Example 2

The copper layer treated according to Example 1 was processed in an aqueous solution of pH 8.9 of 10 g/L dimethylamine borane for 10 minutes. After reduction treatment, the copper layer was immersed in a dilute 2% sulfuric acid solution for 1 minute. Also, the neutralized copper layer was coated with an aqueous solution of pH 12.1 of 0.2 g/L 2-mercaptopbenzothiazole. The processed and treated copper layer was dried at 325° F for 30 minutes, and then laminated with dielectric bonding sheets.

25 Example 3

A copper metal layer was oxidized as in Example 1. The oxide treated copper layer was processed in an aqueous solution of pH 8.9 of 10 g/L dimethylamine borane for 10 minutes. After reduction, the copper layer was immersed in an aqueous solution containing 2 g/L citric acid to effect neutralization. The neutralized copper layer was dipped for 10 minutes in an aqueous solution at pH 12.1 that contained 0.2 g/L mercapt benzothiazol and 1.5 g/L NaOH. The reduced and passivated copper layer was dried at 325° F for 30 minutes, and then laminated with dielectric bonding sheets.

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Example 4

A copper metal layer was oxidized to a black oxide by dipping it in a solution at 200° F for 4 minutes wherein the solution comprised 72g/L sodium chlorite and 90g/L sodium hydroxide. The layer of copper was removed and subjected to a two minute running water rinse.

Example 5

The oxidized copper layer of Example 4 was dipped for 10 minutes in an aqueous solution of pH 8.9 that contained 10 g/L dimethylamine borane. Within 5 minutes after reduction, the copper layer was immersed in an aqueous 2% vol/vol sulfuric acid solution. Within 5 minutes, the reduced copper layer was immersed for 10 minutes in an aqueous solution of pH 12.5 containing 0.2 g/L 2-mercaptobenzothiazole and 1.5 g/L NaOH. The reduced and passivated copper layer was dried at 325° F for 30 minutes, and then laminated with dielectric bonding sheets.

Example 6

A copper metal layer was oxidized as in Example 1. The oxide treated copper layer was processed in an aqueous solution of pH 8.9 of 10 g/L dimethylamine borane for 10 minutes. After reduction, the copper layer was immersed in a dilute 2% sulfuric acid solution for 1 minute. The neutralized copper layer was immersed for 10 minutes in an aqueous solution of 0.5% by volume coco imidazoline. The reduced and passivated copper layer was dried at 250° F for 30 minutes, and then laminated with dielectric bonding sheets.

Example 7

A copper metal layer was oxidized as in Example 6. The oxidized copper layer was immersed for 10 minutes in an aqueous solution of pH 8.9 and containing 10 g/L dimethylamine borane. After reduction, the copper layer was immersed in a

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dilute 2% sulfuric acid solution for 1 minute. Within 5 minutes, the reduced copper layer was coated for 10 minutes with an aqueous solution of pH 10.65 and containing sodium tolyltriazole. The reduced and passivated copper layer was dried at 280° F for 30 minutes, and then laminated with dielectric bonding sheets.

Because the invention may be copied without copying the precise details of the preferred embodiment, the following claims particularly point out and distinctly claim the subject matter which the inventor regards as his invention and wishes to protect.

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I claim:

1. An improved method for bonding a layer of copper or copper alloy to a polymer layer comprising the steps of:

5 (a) oxidizing a surface of a layer of copper or copper alloy;

(b) reducing the oxidized surface of the copper or copper alloy to a lower oxidation state or a mixture of lower oxidation states;

10 (c) passivating the reduced surface of the copper or copper alloy; and

(d) bonding the reduced and passivated surface of the copper or copper alloy to a polymer layer.

15 2. The improved method of Claim 1 wherein the oxidizing step comprises treating the surface of the layer of copper or copper alloy with an aqueous solution containing an oxidizing agent and having a pH of 8 or greater.

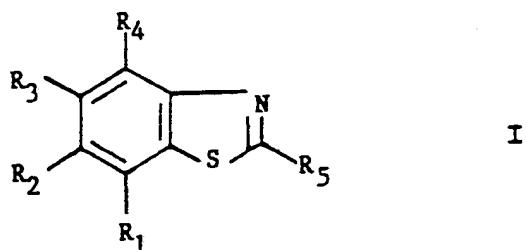
20 3. The improved method of Claim 1 wherein the reducing step comprises treating the oxidized surface of the copper or copper alloy with an aqueous solution having a pH of 7 or greater and containing an aldehyde, a hydrazine, 25 a hypophosphite, a sodium borohydride, or an amine borane represented by a general formula $BH_3 \cdot NHRR'$, where R and R' are each -H or -CH₃ or -CH₂CH₃.

30 4. The improved method of Claim 3 wherein the aqueous solution having a pH greater than 7 contains dimethylamine borane.

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5. The improved method of Claim 1 wherein the passivating step comprises treating the reduced surface of the copper or copper alloy with an aqueous solution comprising an effective amount of one or more compounds selected from the group consisting of hydroquinone, resorcinol, benzotriazole, imidazoline, sodium tolyltriazole, coco imidazoline, 2-ethylhexyl mercaptoacetate and a compound of the formula:

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wherein R₁, R₂, R₃, and R₄ may be the same or different and are -H, or -CH₃, or -CH₂CH₃; and

wherein R₁ and R₂ act together to form

-CH=CH-CH=CH-; or

wherein R₂ and R₃ act together to form

-CH=CH-CH=CH-; or

wherein R₃ and R₄ act together to form

-CH=CH-CH=CH-; and wherein R₅ is -OH, -SH, or a

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corresponding sodium, potassium, lithium, or ammonium salt thereof.

25

6. The improved method of Claim 5 wherein the passivating solution comprises an effective amount of the compound of Formula I in a solvent comprising a C₁ to C₆ alcohol or glycol or a cellosolve (ethylene glycol monoethyl ether) or a polyethylene glycol.

7. The improved method of Claim 6 wherein the solvent further includes water.

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8. The improved method of Claim 5 wherein the passivating solution comprises is a solution of 2-mercaptobenzothiazole or its corresponding sodium, potassium, lithium or ammonium salt.

9. The improved method of Claim 8 wherein the passivation solution comprises an aqueous solution containing sodium-2-mercaptobenzothiazole.

10 10. An improved method for preparing the surface of a layer of copper or a copper alloy for bonding to a polymer layer comprising the steps of:

15 (a) oxidizing a surface of a layer of copper or copper alloy;

(b) reducing the oxidized surface of the copper or copper alloy to a lower oxidation state or a mixture of lower oxidation states; and

20 (c) passivating the reduced surface of the copper or copper alloy.

11. The improved method of Claim 10 wherein the oxidizing step comprises treating the surface of the layer of copper or copper alloy with an aqueous solution containing an oxidizing agent and having a pH of 8 or greater.

30 12. The improved method of Claim 10 wherein the reducing step comprises treating the oxidized surface of the copper or copper alloy with an aqueous solution having a pH of 7 or greater and containing an aldehyde, a hydrazine, a hypophosphite, a sodium borohydride, or an amine borane represented by a general formula $BH_3 \cdot NHRR'$, where R and R' are each -H or -CH₃ or -CH₂CH₃.

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13. The improved method of Claim 12 wherein the aqueous solution having a pH greater than 7 contains dimethylamine borane.

5 14. The improved method of Claim 10 wherein the passivating step comprises treating the reduced surface of the copper or copper alloy with an aqueous solution comprising an effective amount of one or more compounds selected from the group consisting of hydroquinone, resorcinol, 10 benzotriazole, sodium tolyltriazole, coco imidazoline, 2-ethylhexyl mercaptoacetate and a compound Formula I.

15 15. The improved method of Claim 14 wherein the passivating solution comprises an effective amount of the compound of Formula I in a non-aqueous solvent wherein the non-aqueous solvent is a C₁ to C₆ alcohol or a glycol or cellosolve (ethylene glycol monoethyl ether) or a polyethylene glycol.

20 16. The improved method of Claim 15 wherein the solvent further includes water.

25 17. The improved method of Claim 14 wherein the passivating solution is a solution of 2-mercaptobenzothiazole or its corresponding sodium, potassium, lithium or ammonium salt.

18. The improved method of Claim 17 wherein the passivating solution comprises an aqueous solution containing sodium-2-mercaptobenzothiazole.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/08778

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC⁵ C 23 C 18/38, H 05 K 3/46

IPC :

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁵	C 23 C, H 05 K, C 23 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4 775 444 (JOHN L. CORDANI) 04 October 1988 (04.10.88), see abstract; claims 1-14 (cited in the application). --	1-18
A	EP, A1, 0 189 913 (HITACHI, LTD.) 06 August 1986 (06.08.86), see abstract; claims 1-9. ----	1-18

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

09 July 1992

Date of Mailing of this International Search Report

04 AUG 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

PCT/US 91/08778 SAE 55002

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Orientierung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

au rapport de recherche international relatif à la demande de brevet international n°

ANNEXE

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4775444	04-10-88	AU A1 16255/88 CA A1 1271264 EP A1 331684 JP T2 2500555 WO A1 8901990	31-03-89 03-07-90 13-09-89 22-02-90 09-03-89
EP A1 189913	06-08-86	DE CO 3661427 EP B1 189913 JP A2 61176192 JP B4 3050431 US A 4642161	19-01-89 14-12-88 07-08-86 01-08-91 10-02-87